

Adsorption of fluorobenzene onto granular activated carbon: Isotherm and bioavailability studies

M.F. Carvalho, A.F. Duque, I.C. Gonçalves, P.M.L. Castro *

Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Rua Dr. António Bernardino de Almeida, 4200-072 Porto, Portugal

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Abstract

The adsorption of a recalcitrant fluoroaromatic compound, fluorobenzene (FB), onto granular activated carbon (GAC) was evaluated. The respective isotherm was obtained and the Langmuir, Freundlich and Redlich–Peterson models were fitted to the experimental data, with the Redlich–Peterson model giving the best fitting. Freundlich model also provided a good fit but the Langmuir model could not adequately fit the experimental data, especially at high FB concentrations. Maximal adsorption capacity of FB onto GAC was found to be 388 mg of FB per gram of GAC. The reversibility of the adsorption of FB onto GAC was investigated, both in the absence and presence of microorganisms. Abiotic desorption of FB occurred to a small extent (between 3% and 22%, for amounts of FB initially adsorbed to the GAC between 37 and 388 mg g⁻¹), and bioregeneration of GAC was shown to occur when the matrix was exposed to a FB degrading culture, with 58–80% of the adsorbed FB being biodegraded. A residual amount of FB showed not to be bioavailable, suggesting that part of the adsorbed FB may be irreversibly bound. The fraction of the non-bioavailable FB increased at higher amounts of adsorbed FB, from 19% to 33%. The results indicate that the GAC employed in this study has a good capacity to adsorb FB and that bioregeneration of this matrix is a feasible process.

Introduction

Activated carbon (AC) based biofilm reactors constitute a successfully applied technology for the treatment of aqueous effluents contaminated with aromatic pollutants (Speitel et al., 1989; Jaar and Wilderer, 1992; Klecka et al., 1996; Khodadoust et al., 1997; Carvalho et al., 2001). These reactor systems remove organic matter through a combination of physical adsorption and biological transformation, contributing to an enhanced quality of the effluent characteristics. A major benefit of AC in biological systems is related to its capacity to act as a buffer, due to the high adsorptive characteristics of this matrix. Shock loads of pollutants may be temporarily adsorbed and later biodegraded by the microbial population, thus allowing more time for the

biofilm microorganisms to effectively mineralise the compounds (Abu-Salah et al., 1996; Khodadoust et al., 1997; Carvalho et al., 2001). Here, the adsorbed compounds become available for microbial degradation in a process known as bioregeneration. Bioregeneration leads to the renewal of the adsorptive capacity of AC, as microorganisms, while degrading the adsorbed compounds, release the adsorption sites, which can be then occupied by other organic molecules in the bulk solution (Rice and Robson, 1982). This process has been shown to occur in different AC types (Chudyk and Snoeying, 1984; Voice et al., 1992; Jonge et al., 1996a).

Halogenated aromatic compounds are important environmental pollutants of soil, water and air. Fluorinated compounds are among these due to their useful applications, such as aerosol propellants, surfactants, refrigerants, plastics, anesthetics, pesticides, plant growth regulators, medicines, adhesives and fire retardants (Key et al., 1997).

* Corresponding author. Tel.: +351 225580059; fax: +351 225090351.
E-mail address: plcastro@esb.ucp.pt (P.M.L. Castro).

The improper disposal together with the chemical inertness and hydrophobicity of many of these compounds led to their persistence in the environment and to the necessity of finding effective remediation technologies for their removal.

Very few studies are available on the degradation of fluorobenzene (FB), a recalcitrant fluoroaromatic compound. The potential sources of environmental release of FB are related to its main use as a solvent in the pharmaceutical industry, as an insecticide and as a reagent for plastic and resin polymers production. Only recently the microbial degradation of this compound as a single carbon and energy source was reported (Carvalho et al., 2002, 2005). The present paper reports on the adsorption capacity and equilibrium characteristics of FB onto granular activated carbon (GAC). The GAC sorption capacity for this compound was evaluated using the adsorption isotherm technique and the Langmuir, Freundlich and Redlich–Peterson models were fitted to the experimental data. In addition, the bioavailability of the adsorbed FB for further microbial degradation was evaluated.

Methods

Adsorbent and reagents

The experiments were conducted with thermally activated peat-based GAC (8–20 mesh, 0.85–2.4 mm particle size, surface area 600–800 m² g⁻¹) obtained from Sigma Chemical Co., St. Louis, USA. Prior to use, GAC was washed several times with deionised water to remove carbon fines, dried in an oven at 105 °C, and sterilised by autoclaving.

All reagents used were of the highest purity grade available (Sigma–Aldrich Chemie, Steinheim, Germany; Merck, Darmstadt, Germany).

Bacterial inoculum for bioavailability studies

A pure bacterial culture (designated as F11), capable to grow on FB as a sole carbon and energy source (Carvalho et al., 2005), was used in this work to test the bioavailability of FB adsorbed to the GAC. Strain F11 was grown in sealed flasks filled to one-third of their volumes and containing a minimal salts liquid medium (MM) (Caldeira et al., 1999) supplied with 100 mg l⁻¹ of FB. The cultures were incubated on a rotatory shaker at 150 rpm and 25 °C. Growth was monitored at 600 nm and FB biodegradation was followed through the measurement of fluoride ion liberation. Late-exponential FB-grown cells of strain F11 (containing no FB in solution) were used as inocula for the bioavailability studies.

Equilibrium FB adsorption studies

The adsorption of FB to GAC was determined by incubating a series of 100 ml Schott flasks containing 0.2 g

GAC and completely filled with MM supplemented with FB at 50–1500 mg l⁻¹. A control flask, containing a FB solution at 200 mg l⁻¹ and no GAC, was prepared to investigate possible losses of this compound from causes other than GAC adsorption. The flasks were closed with gas-tight rubber stoppers coated with a Teflon layer and placed in a rotatory shaker at 200 rpm and 25 °C. The adsorption of FB to the GAC was monitored after a 96 h period, since preliminary studies revealed that this contact time period was sufficient to achieve adsorption equilibrium. The amount of unbound FB was analysed in the samples supernatant by Gas Chromatography (GC). To avoid losses of FB, the flasks were sampled without their opening, through sterilised glass syringes. The experiment was repeated twice and only mean values are presented in this study.

Bioavailability studies

To evaluate the bioavailability of FB, the GAC resultant from the adsorption experiments was transferred to a series of 500 ml Schott flasks, to which 100 ml of fresh MM was added. Before inoculating the flasks with strain F11, the reversibility of FB adsorption was abiotically evaluated under the same conditions used for the FB adsorption studies, i.e. 200 rpm, 25 °C, and along the same time period, 96 h, which revealed to be sufficient to achieve desorption equilibrium. After this period, the medium was removed from the flasks and replaced by 100 ml of a late-exponential F11 culture, pre-grown on FB, with a biomass concentration of ca. 0.1 g l⁻¹. A non-inoculated flask from the same experimental series was used as a control to verify the abiotic desorption and/or degradation of FB during the bioavailability study period. The flasks were incubated statically, to allow biofilm development, for 32 days at 25 °C. Fluoride release and FB concentration were periodically measured in the samples supernatant. To avoid losses of FB, the flasks were sampled without their opening, through sterilised glass syringes.

Analytical techniques

FB was analysed by GC on a Varian Star 3400 CX model equipped with a CP-Wax 52 CB capillary column (50 m long × 0.25 mm i.d.; Chrompack International B.V., Middelburg, The Netherlands), and a flame ionization detector (FID) (FB method detection limit 0.7 mg l⁻¹). Samples were analysed under a temperature regimen starting at 50 °C for 2 min, increasing to 150 °C at a rate of 25 °C/min and reaching a final temperature of 250 °C at a rate of 50 °C/min. Injector and detector temperatures were 250 °C. Culture samples (4.5 ml) were extracted with 2 ml diethylether containing mesitylene as internal standard, by vortexing the extraction tube for 1 min at maximum speed. The ether layer was analysed by split injection of 1 µl samples in the GC.

The concentration of fluoride ions in culture supernatants was measured with an ion-selective combination

electrode (model CH-8902, Mettler-Toledo GmbH, Urdorf, Switzerland), which was calibrated with NaF (0.1–10 mM) in MM.

Results

FB adsorption isotherm

The capacity of GAC to adsorb FB was evaluated through the determination of the respective isotherm. For this, different concentrations of FB were supplied to flasks containing equal amounts of GAC. A control flask, without the addition of GAC, was set-up to ascertain for losses of FB, showing no losses of this compound during the time course of the experiment. The experimental and calculated adsorption isotherms of FB onto GAC at pH 7 and 25 °C are shown in Fig. 1, with model parameters listed in Table 1. The Freundlich, Langmuir and Redlich–Peterson models were fitted to the experimental data.

The Freundlich model is described by the equation:

$$q_e = KC_e^{1/n} \quad (1)$$

where C_e is the equilibrium concentration of the adsorbate (mg l^{-1}) and q_e is the amount of adsorbate adsorbed per unit weight of the adsorbent (mg g^{-1}). Parameters K and

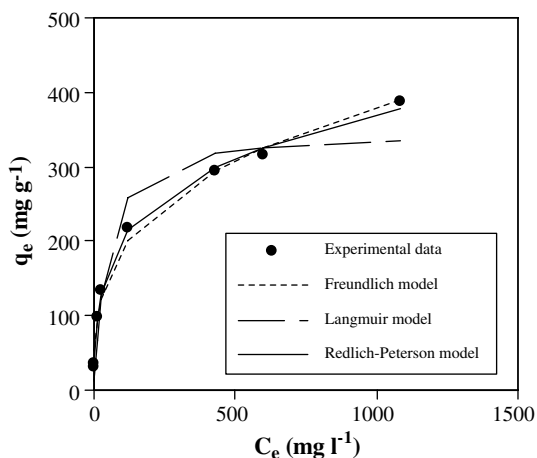


Fig. 1. Experimental and predicted adsorption isotherms of FB onto granular activated carbon at 25 °C and pH 7.

Table 1
Adsorption model parameters determined for FB at pH 7 and 25 °C

Model	Parameter	Calculated value	R^2
Freundlich	$K (\text{mg g}^{-1}) (\text{mg l}^{-1})^{-1/n}$	46.77	0.9894
	$1/n$	0.30	
Langmuir	$K (\text{mg g}^{-1})$	348.57	0.9448
	$a (\text{l mg}^{-1})$	0.02	
Redlich–Peterson	$K (\text{l g}^{-1})$	44.54	0.9979
	$a (\text{l mg}^{-1})^b$	0.64	
	b	0.76	

n are Freundlich constants, whereby K is a measure of the adsorption capacity and n a measure of the adsorption intensity (Tanada et al., 1999).

Langmuir model can be described by the following equation:

$$q_e = \frac{KaC_e}{1 + aC_e} \quad (2)$$

In Eq. (2), K and a are the Langmuir isotherm constants related to maximum adsorption capacity and energy of adsorption, respectively. C_e and q_e have the same definitions as in Eq. (1).

Redlich–Peterson model describes a three-parameter isotherm, which combines elements of the Langmuir and Freundlich isotherms in a single equation:

$$q_e = \frac{KC_e}{1 + aC_e^b} \quad (3)$$

where K and a are the Redlich–Peterson isotherm constants and b the Redlich–Peterson isotherm exponent, which lies between 0 and 1. C_e and q_e have the same definitions as in Eq. (1).

The parameters of the adsorption models listed above were determined by non-linear regression analysis using a statistical software STATISTICA™ version 6.0 (Statsoft®, Tulsa, OK, USA), which utilizes the Marquardt–Levenberg algorithm for the least squares function minimisation.

From the results shown in Fig. 1, it is possible to observe that the equilibrium sorption capacity of the GAC for FB increased with increasing the initial FB concentration, which may be explained by a higher probability of contact between the matrix and the compound. The increase in the adsorption capacity was most significant for initial FB concentrations between 50 and 800 mg l^{-1} (corresponding to equilibrium concentrations of 1.7–426 mg l^{-1} of FB). Further increase in the initial FB concentrations resulted in a less significant increase on the adsorption capacity, with a maximal adsorption capacity of 388 mg of FB per gram of GAC being achieved.

The experimental data were best fitted to the Redlich–Peterson isotherm, for which the highest coefficient of correlation was obtained (Table 1), although a good fit was also provided by the Freundlich isotherm. The Langmuir model did not reproduce equilibrium data satisfactorily, especially for high concentration ranges.

The magnitude of the Freundlich exponent, $1/n$, is an indicator of the favourability of adsorption, with exponent values between $1 < n < 10$ showing a beneficial adsorption (Treybal, 1988; Annadurai et al., 2000). The Freundlich exponent, $1/n$, obtained in this study was 0.3 (corresponding to a n value of 3.3) (Table 1), indicating a favourable FB adsorption. The Redlich–Peterson isotherm exponent, b , calculated as 0.76 (Table 1), is also indicative of a favourable adsorption of FB to GAC (Aksu and Kabasakal, 2004). In the Langmuir isotherm, the constant a can also be used as an indicator of the favourability of adsorption through the determination of the dimensionless

separation factor (Zeng et al., 2004). The dimensionless separation factor is defined as

$$R_L = \frac{1}{1 + aC_i} \quad (4)$$

where a is the Langmuir constant and C_i is the initial solute concentration (Weber and Chakraborti, 1974). R_L values between 0 and 1 are indicative of favourable adsorption. Based on the Langmuir constant, a , presented in Table 1, the R_L values obtained for the initial FB concentrations between 50 and 1500 mg l⁻¹ were in the range of 0.5–0.03, indicating also a favourable adsorption of FB to GAC.

In contrast to the Freundlich and Redlich–Peterson isotherms, the Langmuir model provides information on the saturation behaviour of the adsorbent, with the K parameter representing the total adsorption capacity of the adsorbent (Aksu and Kabasakal, 2004). In this study, this parameter was calculated as 348.57 mg of FB per gram of GAC (Table 1), a value that is reasonably close to the experimental one (388 mg of FB per gram of GAC). In the Freundlich and Redlich–Peterson isotherms, the K parameter gives an indication on the extent of adsorption. For both isotherms, the K parameter calculated was very similar (46.77 for the Freundlich isotherm and 44.54 for the Redlich–Peterson isotherm-Table 1), and indicate a high capacity of the GAC to adsorb FB.

Bioavailability of the adsorbed FB

The bioavailability of FB adsorbed to GAC was investigated in batch systems. Prior to bioavailability studies, the GAC resultant from the adsorption experiment was used to investigate the occurrence of abiotic desorption. The results from this experiment revealed that a small percentage of the FB adsorbed to the GAC was abiotically desorbed. From 37 to 388 mg of FB per gram of GAC initially adsorbed to the GAC matrix, 1–86 mg g⁻¹ (between 3% and 22%) was released back to the culture medium (Fig. 2).

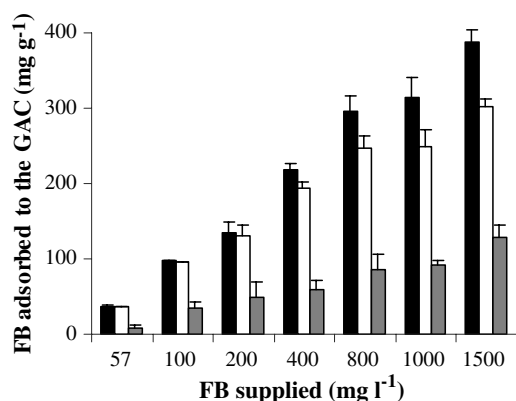


Fig. 2. Reversibility of FB adsorption. (■) FB adsorbed after 96 h; (□) FB remaining adsorbed after a 96 h desorption period, under abiotic conditions; (▒) FB remaining adsorbed after addition of a F11 culture. Bars represent standard deviations ($n = 2$).

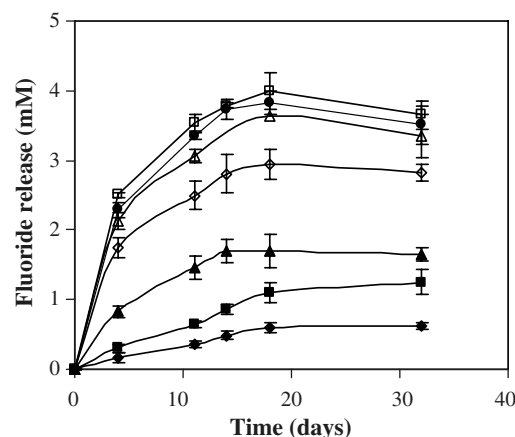


Fig. 3. Utilization of the adsorbed FB by a FB degrading culture. FB loading (after the abiotic desorption studies): (◆) 36 mg g⁻¹; (■) 96 mg g⁻¹; (▲) 130 mg g⁻¹; (◇) 193 mg g⁻¹; (△) 246 mg g⁻¹; (●) 250 mg g⁻¹; (□) 302 mg g⁻¹. The inoculum was supplied to an optical density (at 600 nm) of approximately 0.21, from a F11 culture pre-grown on FB. Bars represent standard deviations ($n = 2$).

Inoculation of the GAC containing flasks with a FB degrading culture indicated that the organic compound became bioavailable (Figs. 2 and 3). The amount of FB degraded by the inoculated culture was monitored through the release of fluoride ion to the medium (Fig. 3), and FB was never detected in the liquid media. FB adsorbed to the GAC became slowly bioavailable and its degradation occurred along a period of about 18 days. The results revealed that from the 36–302 mg of FB loaded per gram of GAC (corresponding to 0.75–6.28 mM of FB in solution), ca. 29–174 mg g⁻¹ (58–80%) were degraded by the F11 culture (Fig. 2). The amount of fluoride release increased with increasing FB loading. As illustrated in Fig. 2, not all the FB adsorbed to the GAC was available for microbial degradation, as for the different FB concentrations a residual amount of FB remained adsorbed to the GAC (between 7 and 128 mg g⁻¹ for initial GAC loads of 37–388 mg of FB per gram of GAC), suggesting that part of the adsorbed FB may be irreversibly bound.

An uninoculated flask was used as a control to investigate the extent of abiotic FB desorption and degradation during the bioavailability study period. No abiotic degradation occurred in the control flask, as indicated by the absence of fluoride release, and the amount of FB desorbed abiotically was very low (Fig. 4), indicating that the desorption of FB from GAC in the presence of the FB degrading culture was enhanced by the microorganisms. In the control flask, the desorption equilibrium was achieved after a period of 96 h, which is consistent with the data obtained in the abiotic desorption experiment. Furthermore, the extent of FB desorption that occurred in this flask (0.06 mM, corresponding to 3.89 mg of FB per gram of GAC) is similar to that observed in the abiotic desorption experiment, for a supplied FB concentration of 2 mM (Fig. 2).

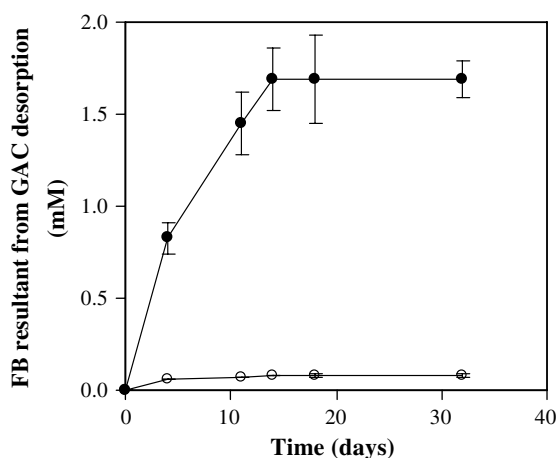


Fig. 4. Quantity of FB desorbed from the GAC under abiotic conditions (○) and on the presence of a FB degrading culture (based on biodegradation determined from fluoride release) (●). Data of the experiment was obtained for an initial FB amount loaded onto the GAC corresponding to 2 mM in solution. Bars represent standard deviations ($n = 2$).

Discussion

AC adsorption and biological degradation constitutes a common approach to treat recalcitrant pollutants, which are usually slowly biodegradable. Before employing such biological type systems it is important to assess whether the AC matrix has a good capacity to adsorb the pollutants, and if the adsorbed compound can be available for microbial degradation, the latter leading to the extension of the AC life through the bioregeneration process.

In this study, the capacity of GAC to adsorb FB was evaluated through the determination of the respective isotherm. Isotherms are useful in which they describe the equilibrium of a given solute between the liquid and solid phases. The most common models used to describe the adsorption of organic and inorganic compounds onto different matrices, including activated carbon, are the Freundlich, Langmuir and the Redlich–Peterson (Armenante et al., 1996; Suzuki, 1997; Ng et al., 2003). The Freundlich isotherm (Freundlich, 1906) is an empirical model, which is often used to describe the carbon-sorption of organic com-

pounds from liquid solutions in single solute systems. Langmuir isotherm assumes monolayer adsorption over a homogenous adsorbent surface and no remotion of adsorbate on the surface (Langmuir, 1918), while Redlich–Peterson model (Redlich and Peterson, 1959) is a three-parameter isotherm, which does not follow ideal monolayer adsorption and can be used to represent adsorption equilibrium over a wide concentration range. In this study, the model that best described the obtained experimental data was the Redlich–Peterson model, with the Freundlich model also providing a good fit. The Langmuir model could not fit well the experimental data, which may be attributed to the fact that the adsorption sites of the GAC are not identical and energetically equivalent and that multiple-layer adsorption may occur in this system (Chern and Chien, 2002). In spite of this, the Langmuir constant, K , predicted reasonably the maximum amount of FB adsorbed per gram of GAC (388 mg of FB per gram of GAC against the K value predicted by the Langmuir isotherm of about 349 mg of FB per gram of GAC).

The analysis of the parameters determined for each isotherm model (Table 1), revealed concordant results with respect to the capacity, intensity and favourability of GAC adsorption, with GAC showing a good adsorption capacity and affinity for FB. Due to the lack of adsorption studies in the literature for this compound, the isotherm parameters determined here were compared to values available in the literature for the adsorption of some other (halo)aromatic compounds onto activated carbon (Table 2). Only the Freundlich and Redlich–Peterson isotherm models were considered for comparison because these models provided better fitting results not only in this study but also in the literature reports listed in Table 2.

The Freundlich constants, K and $1/n$, obtained in the literature for the compounds 2,4-dichlorophenoxy-acetic acid, phenol, resorcinol and catechol were very similar to the ones obtained in this study, indicating similar capacities and intensities of GAC adsorption. However, the K value reported in the literature for the chlorinated analogue of FB (chlorobenzene) was about two times higher than the one obtained in this study for FB, indicating a higher capacity of the activated carbon to adsorb chlorobenzene.

Table 2
Isotherm constants for various organic compounds adsorbed onto activated carbon

Compound	Matrix (surface area)	Isotherm model					Reference
		Freundlich		Redlich–Peterson			
		K	$1/n$	K	a	b	
2,4-Dichlorophenoxyacetic acid	GAC (600–650 m ² g ^{−1})	42.48	0.48	18.42	0.08	0.81	Aksu and Kabasakal (2004)
Phenol	GAC (ca. 579 m ² g ^{−1})	40.09	0.23	ND	ND	ND	Kumar et al. (2003)
Resorcinol	GAC (ca. 579 m ² g ^{−1})	34.83	0.23	422.87	11.92	0.77	Kumar et al. (2003)
Catechol	GAC (ca. 579 m ² g ^{−1})	42.40	0.20	93.22	1.83	0.83	Kumar et al. (2003)
Chlorobenzene	Activated carbon (NA)	100	0.35	ND	ND	ND	Dobbs and Cohen (1980)
4-Chlorophenol	Activated carbon pellets (ca. 1100 m ² g ^{−1})	1.00	0.85	ND	ND	ND	Armenante et al. (1996)

NA = Not available.

ND = Not determined.

Nonetheless, the intensity of adsorption of these two compounds was very similar, as indicated by the $1/n$ values. Comparing to the adsorption of 4-chlorophenol onto activated carbon pellets, the GAC used in this study showed a higher capacity and affinity to adsorb FB, in spite of its smaller surface area.

Despite the similar Freundlich constants values observed for the compounds 2,4-dichlorophenoxy-acetic acid, phenol, resorcinol and catechol, and for FB presented in this study, the values obtained for the Redlich–Peterson constants, K and a , were different from those reported in the literature, varying in order of magnitude among the compounds. This may be due to the fact that the Redlich–Peterson model considers not only heterogeneous adsorption surfaces but also the possibility of multilayer adsorption (Baker and Khalili, 2004), and different mechanisms of adsorption may be associated to each compound. Nevertheless, the magnitude of the Redlich–Peterson exponent, b , reported in the literature studies is very similar to the one obtained for the FB adsorption onto GAC, indicating favourability of adsorption.

The reversibility of FB adsorption onto GAC was investigated in this study, both in the absence and in the presence of microorganisms. In spite of the little contribution of the abiotic process for FB desorption from the GAC, which constitutes an advantage in bioreactor systems regarding the effluent quality, bioregeneration of the matrix was shown to occur when a FB degrading culture (F11 culture) was placed in contact with it. Other GAC adsorbed aromatic compounds were also found to be partially or completely bioregenerated (Speitel and Digiano, 1987; Hutchinson and Robinson, 1990; Jaar and Wilderer, 1992). The main hypotheses concerning bioregeneration include desorption by exoenzymatic reactions (Perrotti and Rodman, 1974) and reversibility of adsorption, implying a desorption step before biodegradation (Schultz and Keinath, 1984; Jonge et al., 1996b; Ha et al., 2000). In the latter hypothesis it is assumed that microorganisms can enhance the desorption of adsorbates from GAC by removing the dissolved compounds in the bulk solution, thus inducing the successive desorption of these compounds, which might also have occurred in the present study.

A residual amount of FB showed to be not bioavailable during the bioregeneration experiments, indicating that part of the adsorbed FB was irreversibly bound. Such feature may lead to more of the GAC sites being irreversibly utilised during adsorption/desorption/bioregeneration cycles. Other authors working with other organic compounds have reported a reduction in the adsorption capacity of bioregenerated GAC through successive cycles (Hutchinson and Robinson, 1990; Ivancev-Tumbas et al., 1998; Nakano et al., 2000). Several theories have been raised concerning the irreversible adsorption of sorbates, and the most common explanation is the occurrence of oxidative polymerization at the GAC surface (Chin et al., 1989; Vidic et al., 1993; Cooney and Xi, 1994). The direct

reaction between the compound molecules and the activated carbon surface, resulting in covalent bonding on the carbon surface is also another possible mechanism (Grant and King, 1990). Bioavailability of the adsorbed compounds is however an important feature when working with systems where adsorption and biodegradation closely interact.

5. Conclusion

The adsorption of FB to and bioregeneration of GAC were evaluated in this study. Based on the obtained results, the following conclusions can be drawn:

- The maximal capacity determined in this study for the adsorption of FB onto GAC was around 388 mg of FB per gram of GAC.
- FB adsorption isotherm was well described by the Redlich–Peterson model with the Freundlich model also providing a good fit. Langmuir model reasonably fitted the experimental data only for low FB concentrations, failing to describe the adsorption process at higher concentrations.
- The FB adsorbed to the GAC (58–80%) was available for microbial degradation, showing that GAC bioregeneration is a feasible process.
- It is demonstrated that GAC has a good capacity to adsorb FB and that bioregeneration is possible to occur in this matrix. It must be, however, stressed that the results obtained are valid for the adsorption of FB when this is presented as an individual compound and that the capacity of GAC to adsorb this compound might be different in the presence of other compounds or biomass.

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